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AUSTINITE: CHEMICAL AND PHYSICAL PROPERTIES IN RELATION TO CONICHALCITE

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ABSTRACT

Most analyses of austinite ($CaZnAsO_4OH$)-conichalcite ($CaCuAsO_4OH$) show little substitution and closely approximate end member compositions. Extensive binary solid solution was found in only one specimen. New crystals of austinite from Durango, Mexico are identical to the type locality material at Gold Hill, Utah. This later yielded $a=7.506 \pm 0.006$, $b=9.046 \pm 0.009$, $c=5.932 \pm 0.006$ Å. These dimensions differ little from conichalcite, $a=7.393 \pm 0.007$, $b=9\ 220 \pm 0.015$, $c=5.830 \pm 0.009$ Å. Compositions in the solid solution may be obtained with an accuracy of ±3 mole % by the regression mole% conichalcite$=5535.165-(932.996 \times c$Å$)$. The crystal structure of austinite is closely related to conichalcite

INTRODUCTION

Austinite $CaZnAsO_4OH$ is classified in the adelite group of minerals which include conichalcite $CaCuAsO_4OH$, adelite $CaMgAsO_4H$, and duftite PbCu AsO_4OH. The four minerals exhibit symmetry $P2_12_12_1$ and according to cell edge may be isostructural. Palache *et al.*, (1951) quote:

	a	*b*	*c*
adelite	7.47	8.94	5.88
conichalcite	7.42	9.20	5.85
austinite	7.43	9.00	5.90
duftite	7.50	9.12	5.90

Available chemical data indicate little solid solution between the four minerals although extensive solution might be expected on the basis of similar symmetry, cell constants, and X-ray diffraction spectra.

Austinite is not currently catalogued in the ASTM Powder Diffraction File. The primary purpose of this investigation is to generate an X-ray diffraction pattern for austinite, refine the cell constants, and examine the possibilities of solid solution of austinite with conichalcite.

Eight specimens were examined in the course of this study (Table 1). Two specimens of austinite were obtained from a new locality at Durango, Mexico and exhibit better crystal form than specimens from the type locality (Gold, Hill Utah). Five specimens were generously supplied by the U. S. National Museum.

TABLE 1. DESCRIPTION OF SPECIMENS EXAMINED IN THIS STUDY

U. Ga. #	USNM #	Name	Locality	Color
A1	—	Austinite	Durango, Mexico	Colorless
A2	—	Austinite	Durango, Mexico	Colorless
A3	—	Austinite	Gold Hill, Utah	Colorless
A4	C5846	Austinite	Gold Hill, Utah	Colorless
A5	R5346	Higginsite (=conichalcite)	Bisbee, Arizona	Bright Green
A6	R5379	Staszicite (=coni/aust.)	Poland	Green Matte
A7	R5608	Barthite (=austinite)	S. W. Africa	Olivine Green
A8	48244	Conichalcite	Utah	Emerald Green

PREVIOUS WORK

Austinite was originally described by Staples (1935) who pointed out the characteristic acicular crystals of low symmetry (222) showing forms {110} and {111}. The crystals which often form rosettes are generally 0.5 mm in length and may be doubly terminated developing a scepter habit. Right and left handed enantimorphs occur but no crystals were observed showing both forms. More recently Williams and de Azevedo (1967) confirmed the crystal morphology on newly discovered crystals from the same type locality at Gold Hill, Utah. They noted many additional forms including {010}, {160}, {130}, {310}, {011}, {101}, {121}, {132}, {131}, {532}, and {431}. The new crystals from Mexico generally show the simple forms {110} {111} in Staples' orientation.

In 1938 Brendler pointed out that the mineral was originally described in 1932 by Ashfeld as brickerite in material from Lomitos, Bolivia. However due to an original erroneous analysis it was not realized until 1936 that brickerite and austinite were the same mineral. Confirmation was based on refractive indices which are as follows (Staples) $X=a=1.759 \pm 0.003$, $Y=b=1.763 \pm 0.003$, $Z=c=1.783 \pm 0.006$.

Strunz (1939) summarized some of the basic chemical properties of austinite and conichalcite. Richmond (1940) provided the first unit cell data (quoted above). Berry (1951) clarified the terminology and listed an X-ray diffraction pattern of conichalcite. Cell constants of *a* 7.40, *b* 9.21, *c* 5.84 Å were obtained and a space group of *Pnam*. Subsequent work by Qurashi, Barnes, and Berry (1953) and Qurashi and Barnes (1963) showed that the space group of conichalcite is actually $P2_12_12_1$.

ORIENTATION OF AUSTINITE

Staples (1935) originally oriented austinite with *c* as the axis of elongation. Richmond (1940) interchanged Staples, *a* and *c* by the matrix

001/010/100 to maintain consistency with other members of the adelite group of minerals. Thus the axis of elongation was assigned to *a*. Confusion arises in Palache *et al.*, (1951) who use Staples' orientation and drawing but assign Richmond's dimensions. Checking of several single crystals on the Buerger precession camera shows that the lengths of the *a* and *c* axes are inconsistent with the drawing and are in fact reversed. Williams and de Azevedo (1967) reverted back to Staples' original orientation in which $a<c<b$. Strunz (1970) retained Staples' orientation. In this paper Richmond's orientation is used in which $c<a<b$, axis of elongation $=a$, long diagonal of rhombic prism $=b$, short diagonal of rhombic prism $=c$. In this orientation comparison with other minerals in the adelite and related descloisite groups is simpler. The dominant forms of the prism is $\{011\}$ rather than $\{110\}$.

X-RAY DIFFRACTION ANALYSIS

Examination of several single crystals on the Buerger precession camera confirmed the space group $P2_12_12_1$. A curious feature was encountered on many of the Mexican specimens. The orientation photographs obtained with unfiltered Mo Kα radiation, no screen, and $\bar{\mu}=10°$ showed doubling of the zero level white radiation streaks. A twinned crystal was suspected but this could not be detected optically under the polarizing microscope. Repeated photographs precessed about the three crystallographic axes yielded a doubling of the pattern but no systematic relationship between axes or between crystals. It was finally concluded that the crystals were twisted slightly, parallel to the axis of elongation. This was confirmed optically. Translation of the crystal perpendicular to ϕ, parallel to the axis of elongation showed a progressive variation of ϕ of up to 10'.

The powder diffraction patterns of specimens A1 through A8 were obtained in a standard Debye-Scherrer camera, radius 114.6 mm. The X-ray patterns for A1, A2, A3 and A4 are identical and are all austinite. The pattern for austinite is markedly similar to that of conichalcite (A8) with only slight deviations in peak positions and intensities. The patterns for A5, A6, A7 fall between austinite and conichalcite and are intermediate compositions. The dominant features of the X-ray patterns are two sets of strong peaks. With Cu Kα radiation the first set occurs at 28.1, 31.9, 34.0 °2θ and the second set at 56.9 and 61.4 °2θ.

Highly complex X-ray patterns were obtained in accord with the low symmetry of the minerals. In austinite A4, 78 diffraction lines could be readily distinguished and the problems of indexing are formidable as many peaks may be assigned non-unique indices. To obtain statistically precise cell constants at least 15 peaks must be indexed uniquely in each

TABLE 2. X-RAY DIFFRACTION DATA FOR AUSTINITE (A4) FROM GOLD HILL, UTAH

Cu $K_{\alpha 1}$ = 1.54051 Å		a = 7.560 ± .066		b = 9.046 ± .009		c = 5.932 ± .006	
I/Io	hkl	d. meas.	d. calc.	I/Io	hkl	d. meas.	d. calc.
5	110*	5.781	5.797	5	122*	2.356	2.353
5	011*	4.987	4.957	½	202*	2.329	2.325
5	111*	4.145	4.136	½	212	2.254	2.252
1	120*	3.860	3.877	4	222*	2.069	2.068
1	200*	3.748	3.756	½	141	2.036	2.035
½	021	3.563	3.596	½	240*	1.939	1.939
1	210*	3.481	3.469	½	400	1.879	1.871
½	121	3.215	3.243	5	331	1.830	1.832
10	201*	3.171	3.171	5	042*	1.79	1.798
1	022	2.955	2.960	3	142	1.747	1.747
1	220	2.890	2.891	3	420*	1.730	1.732
10	130*	2.801	2.800	2	151	1.687	1.687
10	112*	2.637	2.635	9	242	1.616	1.615
5	221	2.592	2.598	2	402*	1.586	1.586
6	131	2.529	2.531	7	060	1.509	1.509
4	022*	2.478	2.478	5	004	1.482	1.480
1	310*	2.416	2.413				

plus another 35 lines with d less than 1.482 Å

* Lines systematically indexed in samples A1 through A8. Cell edges were obtained with these reflections.

mineral. This was achieved by computer refinement (Evans *et al.*, 1963). Eighteen reflections could be systematically indexed in all compositions. These are marked with an asterisk in Table 2. Similar X-ray diffraction data for conichalcite has been reported by Berry (1951). Computer refinement of the cell constants of specimens A4 through A8 representing 5 compositions from austinite to conichalcite are given in Table 3. Four of the five samples approximate end member compositions and this precludes statistical treatment of the relationship between cell edge and composition. The relationship is apparently linear and the composition may be related to the c axis dimension with an accuracy of about ±3 mole percent by the relationship:

$$\text{mole \% conichalcite} = 5535 - [933 \times c\ (\text{Å})]$$

Cu-Zn SUBSTITUTION

The space group of austinite and conichalcite are both $P2_12_12_1$. The cell edges are very similar and the X-ray diffraction patterns are essentially identical with almost no variations in relative intensities. It is as-

TABLE 3. CELL CONSTANTS AND COMPOSITION OF AUSTINITE-CONICHALCITE

Reference	a Å	b Å	c Å	Composition
U. Ga. A4	7.506 ± .006	9.046 ± .009	5.932 ± .066	austinite 100
U. Ga. A7	7.501 ± .004	9.061 ± .005	5.926 ± .005	aust. 97 coni. 3
U. Ga. A6	7.469 ± .023	9.115 ± .008	5.851 ± .009	aust. 31 coni. 67 adel. 2
U. Ga. A5	7.392 ± .004	9.223 ± .010	5.848 ± .006	aust. 2 coni. 98
U. Ga. A8	7.393 ± .007	9.220 ± .015	5.830 ± .009	conichalcite 100
Richmond (1940)	7.43	9.00	5.90	austinite
Richmond (1940)	7.43	9.22	5.86	conichalcite
Strunz (1939)	7.42	9.21	5.84	conichalcite
Berry (1951)	7.40	9.21	5.84	conichalcite

sumed that austinite and conichalcite are closely related crystal structures with Zn replacing Cu.

The crystal structure of conichalcite was refined by Qurashi and Barnes (1963) originally in *Pnma* with final refinement in $P2_12_12_1$. They describe a three-dimensional assemblage of distorted AsO_4 tetrahedra, $CuO_4(OH)_2$ tetragonal bipyramids, and $CaO_7(OH)$ square antiprisms sharing corners and edges.

In the direction parallel to the *c* axis the Cu-Cu distance is 2.92 Å across the shared edge of the $CuO_4(OH)_2$ tetragonal bipyramid of conichalcite. This lattice direction contracts on substitution of Zn for Cu indicating a decrease in the metal-metal distance across the shared edge. There is no sharing of the tetragonal bipyramid in the directions parallel to *a* and *b* and these dimensions expand on substitution of Zn for Cu.

CHEMICAL ANALYSIS

Initial microprobe analysis of rocks containing austinite and conichalcite revealed large variations in the chemistry and the difficulty of distinguishing the minerals from closely related phases. It was necessary to pick out about 20 crystals of each sample under a binocular microscope taking care to select cyrstals of identical color and hopefully, composition. About 15 crystals were used for X-ray diffraction and 5 for microprobe analysis.

Five specimens (A4–A8) were tested for Ca, Mg, Cu, Zn, Fe, Mn, Pb, V, P, and As with a MAC 400S electron microprobe. Using a 100 second integration time and pulse height analysis a detectability limit of 0.1 percent was obtained. Two specimens A4 and A8 are markedly free of substituting elements and repeated microprobe scans showed they are essentially homogeneous. Calculation of their compositions by compari-

TABLE 4. AVERAGE MICROPROBE ANALYSES OF AUSTINITE-CONICHALCITE (Mn, Fe, V, Pb NOT DETECTED)

	A1	A2	A3	A4	A5	A6	A7	A8
CaO	21.1	21.6	21.8	21.5	21.6	21.3	21.5	21.7
ZnO	30.7	30.6	30.6	31.0	.7	9.6	29.9	—
CuO	—	—	—	—	30.1	20.4	1.2	30.7
MgO	.3	.4	.6	—	—	.6	.2	—
As_2O_5	43.9	43.8	43.1	43.6	42.6	42.9	43.8	44.0
P_2O_5	—	—	—	—	1.4	1.2	—	—
Σ*	9.60	96.4	96.1	96.1	96.4	96.0	96.6	96.4
Mole %	$aust_{100}$	$aust_{100}$	$aust_{100}$	$aust_{100}$	$coni_{98}$	$coni_{67}$	$aust_{97}$	$conichalcite_{100}$

* Theoretic $H_2O = 3.5\%$.

son with standards and computation on the IBM 360 utilizing EMPADR 7 (J. Rucklidge, Univ. of Toronto, 1970) yielded near theoretic end member compositions as shown in Table 4. The compositions of the remaining specimens were obtained using A4, A8, apatite, and dolomite as standards.

Substitution of up to 1.4 percent P_2O_5 was observed in conichalcite and up to 0.6 percent MgO in most compositions. However seven of the eight compositions closely approximated the pure end member compositions. Only one specimen yielded evidence of a more extensive solid solution consisting of $austinite_{31}$ $conichalcite_{67}$ $adelite_2$. While the evidence is meager it is logical to assume that complete solid solution exists between austinite and conichalcite. The general absence of binary compositions is probably due to the unavailability of necessary elements at the time of crystal growth.

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